(12) UK Patent Application (19) GB (11) 2 072 665 A

(21) Application No **8107813**
(22) Date of filing **12 Mar 1981**
(30) Priority data
(31) **2013/80**
6929/80
(32) **14 Mar 1980**
16 Sep 1980
(33) **Switzerland (CH)**
(43) Application published
7 Oct 1981
(51) **INT CL³**
C07C 69/612
(52) Domestic classification
C2C 1173 202 220 225 226 227 22Y 234 240 26X 311 313 314 315 31Y 338 339 360 362 364 366 368 36Y 38Y 449 491 623 624 628 652 658 659 65X 662 694 697 699 778 805 80Y AA BU WP
(56) Documents cited
None
(58) Field of search
C2C
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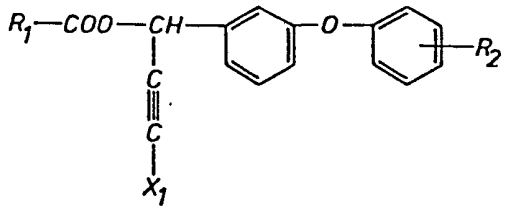
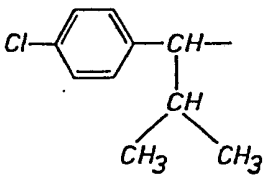
(54) **α-Isopropyl- and α-cyclopropyl-α-(4-chlorophenyl)-acetic acid-α-haloethynyl-m-phenoxybenzyl esters, processes for producing them, and their use for combating insect pests**

(57) α-Isopropyl- and α-cyclopropyl-α-(4-chlorophenyl)-acetic acid-α-haloethynyl-m-phenoxybenzyl esters of the formula



wherein R_1 is



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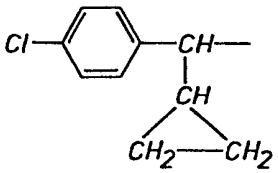

,

R_2 is hydrogen, fluorine, chlorine, bromine, methyl, trifluoromethyl or methoxy, and

X_1 is halogen,

processes for producing them, and their use for combating insect pests.

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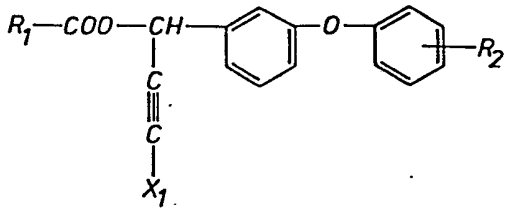
The Chemical formulae appearing in the printed specification were submitted after the date of filing, the formulae originally submitted being incapable of being satisfactorily reproduced.

SPECIFICATION

α-Isopropyl- and α-cyclopropyl-α-(4-chlorophenyl)-acetic acid-α-haloethynyl-m-phenoxybenzyl esters, processes for their production and use

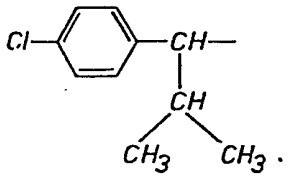
The present invention relates to α-isopropyl- and α-cyclopropyl-α-(4-chlorophenyl)-acetic acid-α-haloethynyl-m-phenoxybenzyl esters, processes for producing them, and their use for combating insect pests.

The present invention provides α-isopropyl- and α-cyclopropyl-α-(4-chlorophenyl)-acetic acid-α-haloethynyl-m-phenoxybenzyl esters of the formula



(I)

wherein R_1 is



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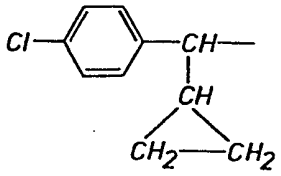
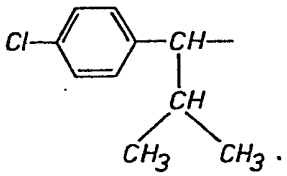


R_2 is hydrogen, fluorine, chlorine, bromine, methyl, trifluoromethyl or methoxy, and
X_1 is halogen.

Halogen in this case is fluorine, chlorine, bromine or iodine, especially however bromine or iodine.

Compounds of the formula I of particular importance on account of their action are those wherein

R_1 is



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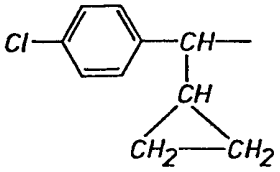
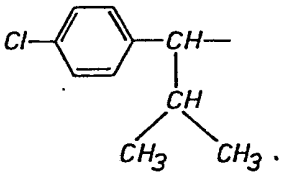


R_2 is hydrogen, fluorine, chlorine, bromine or trifluoromethyl, and
X_1 is bromine or iodine.

More especially of importance however are compounds of the formula I wherein

R_1 is



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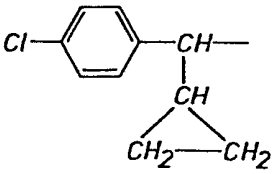
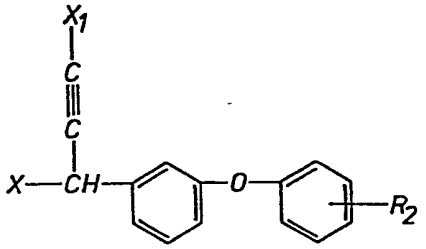
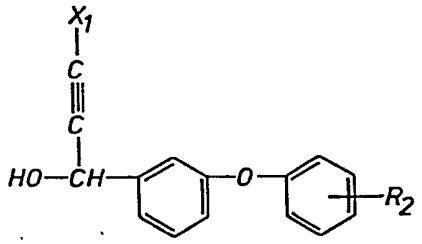
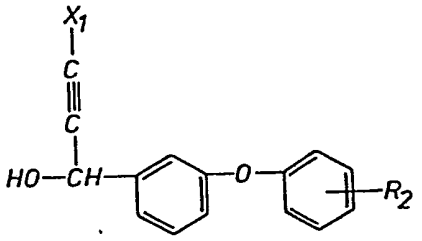


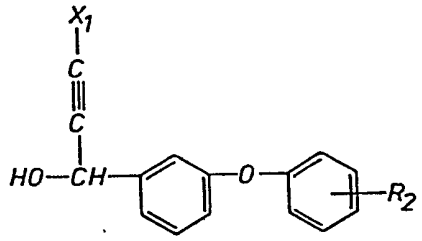
R_2 is hydrogen, and
X_1 is bromine or iodine.

The compounds of the formula I are produced as follows:

1) R_1–COOH (II) +  (III) → acid-binding agent → I,

2) R_1–COX (IV) +  (V) → acid-binding agent → I,

3) R_1–COOH (II) +  (V) → water-binding agent → I

4) R_1–COOR (VI) +  (V) → –ROH → I

In the formulae II to VI, the symbols R_1, R_2 and X_1 have the meanings defined for the formula I.

X in the formulae III and IV is a halogen atom, especially chlorine or bromine; and R in the formula VI is C_1-C_4-alkyl, particularly methyl or ethyl. Suitable acid-binding agents for the processes 1 and 2 are in particular tertiary amines, such as trialkylamine and pyridine, also hydroxides, oxides, carbonates and bicarbonates of alkali metals and alkaline-earth metals, as well as alkali metal alkoholates, for example potassium tert-butylate and sodium methylate. The water-binding agent used for the process 3 can be for example dicyclohexylcarbodiimide. The processes 1 to 4 are performed at a reaction temperature of between −10 and 120°C, usually between 20 and 80°C, under normal or elevated pressure, and preferably in an inert solvent or diluent. Suitable solvents or diluents are for example: ethers and ethereal compounds, such as diethyl ether, dipropyl ether, dioxane, dimethoxyethane and tetrahydrofuran; amides, such as N,N-dialkylated carboxylic acid amides; aliphatic, aromatic as well as halogenated hydrocarbons, especially benzene, toluene, xylenes, chloroform and chlorobenzene; nitriles such as acetonitrile; dimethyl sulfoxide, and ketones such as acetone and methyl ethyl ketone.

The starting materials of the formula II, IV and VI are known, or they can be produced by methods analogous to known methods. The starting materials of the formulae III and V are novel. They are produced in a manner analogous to that described in Tetrahedron Letters, 1448 (1978) (cp. also Example 1A).

If homogeneous optically active starting materials are not used in producing the compounds of the

formula I, these compounds are obtained as mixtures of various optically active isomers. The different isomeric mixtures can be separated by known methods into the individual isomers. It is to be understood that the term 'compounds of the formula I' embraces both the individual isomers and the mixtures thereof.

The compounds of the formula I are suitable for combating various animal and plant pests.

The compounds of the formula I are particularly suitable for combating members of the Arthropoda division, for example of the Insecta class, for example of the orders: Lepidoptera, Coleoptera, Homoptera, Heteroptera, Diptera, Thysanoptera, Orthoptera, Anoplura, Siphonaptera, Mallophaga, Thysanura, Isoptera, Psocoptera and Hymenoptera, and also of the Arachnoidea class, for example of the order Acarina.

In particular, the compounds of the formula I are suitable for combating insects that damage plants, especially insects that damage plants by eating, in crops of ornamental plants and productive plants, particularly in cotton crops (for example against Spodoptera littoralis and Heliothis virescens), and in vegetable crops (for example against Leptinotarsa decemlineata and Myzus persicae). Active substances of the formula I have a very favourable action also against flies, such as Musca domestica, and against mosquito larvae.

The acaricidal action of the compounds of the formula I extends both to plant-damaging Acarina (mites: for example of the families Tetranychidae, Tarsonemidae, Eriophydae, Tyroglyphidae and Glycyphagidae) and to ectoparasitic Acarina (mites and ticks: for example of the families Ixodidae, Argasidae, Sarcoptidae and Dermanyssidae) which do harm to productive animals.

The acaricidal and insecticidal action can be substantially broadened and adapted to suit given circumstances by the addition of other insecticides and/or acaricides. Suitable additives are for example: organic phosphorus compounds, nitrophenols and derivatives thereof, formamidines and chlorinated hydrocarbons.

Compounds of the formula I are combined particularly advantageously also with substances having a synergistic or intensifying effect on pyrethroids. Examples of compounds of this type are, inter alia: piperonylbutoxide, propynyl ethers, propynyl oximes, propynyl carbamates and propynyl phosphonates, 2-(3,4-methylenedioxyphenoxy)-3,6,9-trioxaundecane (Sesamex or Sesoxane), S,S,S-tributyl-phosphorotrithioates and 1,2-methylenedioxy-4-(2-octyl-sulfinyl)-propyl)-benzene.

The compounds of the formula I can be used in a known manner either in an unmodified form or, together with the auxiliaries customarily used in formulation practice, in the form of preparations, for example emulsion concentrates, suspension concentrates, directly sprayable solutions or dilutable solutions, diluted emulsions, wettable powders, soluble powders, dusts or granulates, and also superfine encapsulations in polymeric substances, and the like. The form of application, such as spraying, atomising, dusting, scattering or pouring, is governed entirely by the purpose of application. It is to be ensured however in this respect that the biological behaviour of the active substances of the formula I is not disadvantageously affected by the method of application, or by the type and amount of auxiliaries used for producing the preparation.

The preparations are produced in a known manner, for example by the intimate mixing and/or grinding of the active substances with extenders, such as with solvents or solid carriers, and optionally with the use of surface-active substances (tensides). The solvents used can be: aromatic hydrocarbons, preferably the fractions C_8 to C_{12}, i.e. xylene mixtures or substituted naphthalenes, aliphatic hydrocarbons, such as cyclohexane or paraffins, alcohols and glycols, as well as ethers and esters thereof, strongly polar solvents, such as dimethylsulfoxide or dimethylformamide, and also water. The solid carriers used, for example for dusts and dispersible powders, are mostly natural mineral fillers, such as calcite, talcum, kaolinite, montmorillonite and attapulgite. In order to improve the physical properties, it is also possible to use highly dispersed silicic acids or highly dispersed absorbent polymers. Suitable granulated adsorptive carriers are porous types, for example pumice, broken brick, sepiolite and bentonite; and suitable nonsorbent carriers are for example calcite or sand. There can also be used a great number of pregranulated materials of inorganic or organic nature, such as in particular dolomite, extending to ground plant residues.

Suitable surface-active substances are, depending on the polarity of the active substance of the formula I to be formulated, nonionic, cation-active and/or anion-active tensides having good emulsifying, dispersing and wetting properties; and by tensides are also meant tenside mixtures.

Suitable cation-active tensides are for example: quaternary ammonium compounds, such as cetyl-trimethyl-ammonium bromide. Suitable anion-active tensides are for example: soaps, salts of aliphatic monoesters of sulfuric acid, such as sodium lauryl sulfate, salts of sulfonated aromatic compounds, for example sodium dodecylbenzene-sulfonate, sodium-, calcium- and ammonium-lignin sulfonate, butylnaphthalene sulfonate or a mixture of the sodium salts of diisopropyl- and triisopropylnaphthalene sulfonate. Suitable nonionogenic tensides are for example the condensation products of ethylene oxide with fatty alcohols, for example oleyl alcohol or cetyl alcohol, or with alkylphenols, such as octylphenol, nonylphenol and octylcresol. Other nonionic agents are the partial esters derived from long-chain fatty acids and hexite anhydrides, and the condensation products of these partial esters with ethylene oxide, and lecithins.

The nonionic, anion-active and cation-active tensides commonly used in formulation practice are described in, inter alia, the following publication:
"Mc Cutcheon's Detergents and Emulsifiers Annual", MC Publishing Corp., Ringewood, New Jersey, 1979.

The formulated compositions contain as a rule 0.1 to 99%, particularly 0.1 to 95%, of active substance of the formula I, and 0 to 25% of a tenside, as well as 1 to 99.9% of a solid or liquid additive.

The compositions can also contain further additives, such as stabilisers, defoaming agents, viscosity

regulators, binders, adhesives, as well as fertilisers or other active substances for producing special effects.

The active substances of the formula I can be produced for example as follows (values in % by weight):

Formulation examples for liquid active substances of the formula I

Emulsion concentrates

a)	active substances	20%
	calcium dodecylbenzenesulfonate	5%
	caster oil-polyglycol ether (36 mols of ethylene oxide)	5%
	xylene mixture	70% ;
b)	active substance	40%
	calcium dodecylbenzenesulfonate	8%
	tributylphenol-polyglycol ether (30 mols of ethylene oxide)	12%
	cyclohexanone	15%
	xylene mixture	25% ;
c)	active substance	50%
	tributylphenol-polyglycol ether	4.2%
	calcium dodecylbenzenesulfonate	5.8%
	cyclohexane	20%
	xylene mixture	20% .

Emulsions of any required concentration can be produced from concentrates of this type by dilution with water.

Solutions

a)	active substance	80%
	ethylene glycol monomethyl ether	20 % ;
b)	active substance	10%
	polyethylene glycol 400	70%
	N-methyl-2-pyrrolidone	20% ;
c)	active substance	5%
	epoxidised vegetable oil	1%
	ligroin (boiling limits 160-190°C)	94% ;
d)	active substance	95%
	epoxidised vegetable oil	5% .

These solutions are suitable for application in the form of very small drops.

Granulates

a)	active substance	5%
	kaolin (0.2 - 0.8 mm)	94%
	highly dispersed silicic acid	1%;
b)	active substance	10%
	attapulgite (0.3 - 1 mm)	90%.

The active substance is dissolved in methylene chloride, the solution is sprayed onto the carrier, and the solvent is subsequently evaporated off in vacuo.

Dusts

a)	active substance	2%
	highly dispersed silicic acid	1%
	talcum	97%;
b)	active substance	5%
	highly dispersed silicic acid	5%
	kaolin (finely divided)	90%.

Ready-for-use dusts are obtained by the intimate mixing of the carriers with the active substance.

Formulation examples for solid active substances of the formula I
Wettable powders

a)	active substance	20%
	sodium lignin sulfonate	5%
	sodium lauryl sulfate	3%
	silicic acid	5%
	kaolin	67%;
b)	active substance	60%
	sodium lignin sulfonate	5%
	sodium diisobutylnaphthalenesulfonate	6%
	octylphenol polyglycol ether (7-8 mols of ethylene oxide)	2%
	highly dispersed silicic acid	27%.

The active substance is well mixed with the additives and the mixture is thoroughly ground in a suitable mill. Wettable powders which can be diluted with water to give suspensions of the desired concentration are obtained.

Emulsion concentrate

active substance	10%
octylphenol polyglycol ether (4-5 moles of ethylene oxide)	3%
calcium dodecylbenzenesulfonate	3%
caster oil polyglycol ether (36 moles of ethylene oxide)	4%
cyclohexanone	30%
xylene mixture	50%.

Emulsions of any required concentration can be obtained from this concentrate by dilution with water.

Dusts

a)	active substance	5%
	talcum	95%;
b)	active substance	8%
	kaolin (finely divided)	92%.

Dusts which are ready for use are obtained by mixing the active substance with the carriers, and grinding the mixture in a suitable mill.

Extruder granulate

active substance	10%
sodium lignin sulfonate	2%
carboxymethylcellulose	1%
kaolin (finely divided)	87%.

The active substance is mixed and ground with the additives, and the mixture is subsequently moistened with water. The mixture is extruded and then dried in a stream of air.

Coated granulate

active substance	3%
polyethylene glycol	3%
kaolin (0.3 - 0.8 mm)	94%.

The finely ground active substance is uniformly applied, in a mixer, to the kaolin moistened with polyethylene glycol. Non-dusty coated granulates are obtained in this manner.

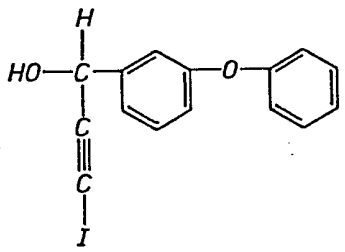
Suspension concentrate

active substance	40%
ethylene glycol	10%
nonylphenol polyglycol ether (15 mols of ethylene oxide)	6%
sodium lignin sulfonate	10%
carboxymethylcellulose	1%
formalin (37% formaldehyde solution)	0.2%
silicone oil in the form of a 75% emulsion	0.8%
mains water	32%.

The finely ground active substance is intimately mixed with the additives. There is thus obtained a suspension concentrate from which can be produced, by dilution with water, suspensions of any concentration required.

EXAMPLES 1 to 6

A) 0.1 mol of methyl lithium dissolved in 50 ml of ether is added dropwise, within 20 minutes at −50 to −60°C under argon, to 10 g of α-ethynyl-m-phenoxybenzyl alcohol in 500 ml of ether. After a further 10 minutes, 5.63 g of iodine dissolved in 100 ml of ether are added dropwise, and stirring is maintained at room temperature for 10 hours. 2 ml of isopropanol are added dropwise, and 20 ml of saturated ammonium chloride solution are then added. The ether phase is washed with saturated sodium chloride solution and dried over magnesium sulfate. The solvent is removed and the residue is chromatographed on silica gel by means of ether/hexane (1:2). The product obtained is the compound of the formula

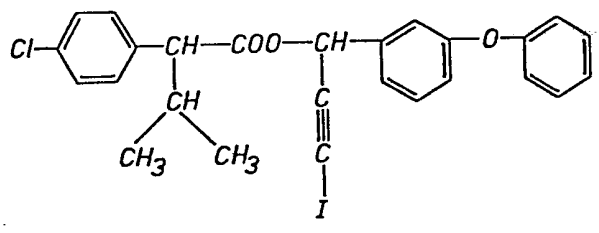


$n_D^{20°} = 1.6237$

NMR spectrum (60 MHz) in CDCl/TMS
δ 3.1 : d 1H
δ 5.4 : d 1H
δ 6.7 – 7.7 : m 9H.

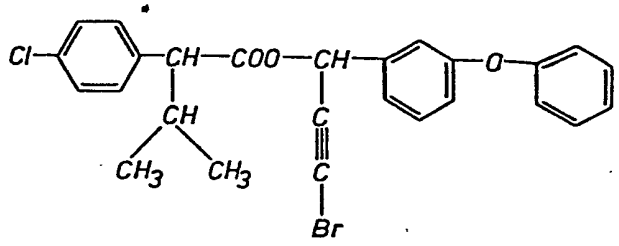
B) Production of α-isopropyl-α-(4-chlorophenyl)-acetic acid-α-iodoethynyl-m-phenoxy-benzyl-ester

A solution of 4.1 g of α-iodoethynyl-m-phenoxy-benzyl alcohol in 20 ml of toluene is added dropwise to an ice-cooled solution of 1.8 g of α-isopropyl-α-(4-chlorophenylacetic acid chloride and 1.2 ml of pyridine in 50 ml of toluene. The reaction mixture is stirred under nitrogen for 16 hours at room temperature, and ether is then added. The ether extract is washed once with water, twice with 2 N hydrochloric acid and three times with saturated sodium chloride solution; it is subsequently dried over sodium sulfate, filtered, and concentrated by evaporation. The product is chromatographed through silica gel with ether/hexane (1:10) as the eluant. There is obtained the compound of the formula

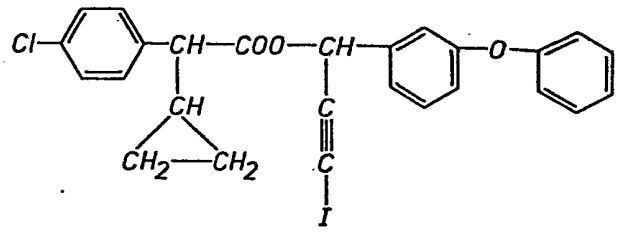


$n_D^{20°}$ at 1,5829

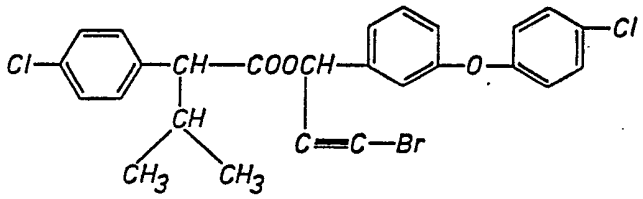
The following compounds are obtained in an analogous manner:



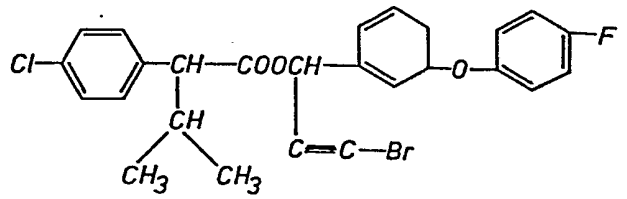
$n_D^{20°} = 1,5827$



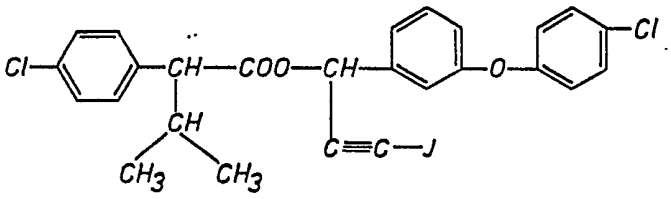
$n_D^{20°} = 1,5729$



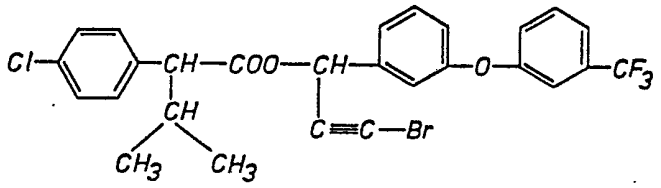
$n_D^{20°} = 1,5779$



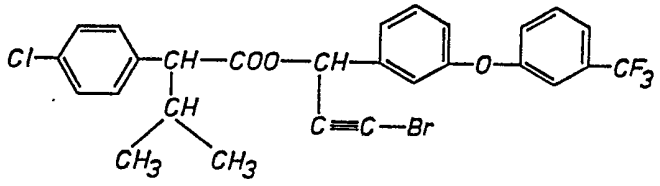
$n_D^{20°} = 1,5703$



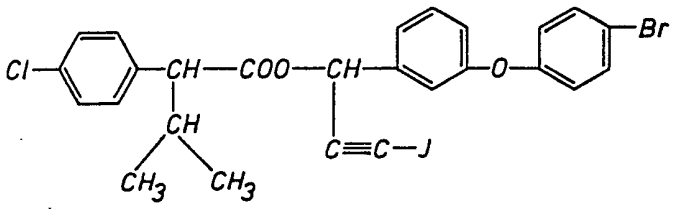
$n_D^{27°} = 1,5953$



$n_D^{20°} = 1,5518$



$n_D^{26°} = 1,5607$



$n_D^{20°} = 1,6027$

EXAMPLE 7

Insecticidal stomach-poison action

Cotton plants were sprayed with aqueous active-substance emulsions or suspensions which contained 100, 200, 400 and 800 parts by weight, respectively, of active substance per 10^6 parts by weight of additives, and which had been prepared in each case from one of the emulsifiable concentrates, wettable powders, granulates or sprays described in the formulation examples given in the foregoing. After drying of the coating, the cotton plants were infested with larvae of Spodoptera littoralis (L_3) and Heliothis virescens (L_3), respectively. The test was carried out at 24°C with 60% relative humidity.

Compounds according to Examples 1 to 6 exhibited in the above test a good insecticidal stomach-poison action against Spodoptera littoralis and Heliothis virescens larvae.

EXAMPLE 8

Acaricidal action

Leaf sections of Phaseolus vulgaris plants infested with Tetranychus urticae larvae were sprayed with aqueous emulsions which contained 100, 200, 400 and 800 parts by weight, respectively, of active substance per 10^6 parts by weight of additives, and which had been prepared from one of the emulsifiable concentrates, wettable powders, granulates or sprays described in the formulation examples given in the foregoing. An assessment was made after two days with respect to the living and dead individuals, respectively, and the minimum concentration required to effect a 100% mortality rate was determined.

Compounds according to Examples 1 to 6 were effective in the above test against larvae of Tetranychus urticae.

EXAMPLE 9

a) *Rhipicephalus bursa*

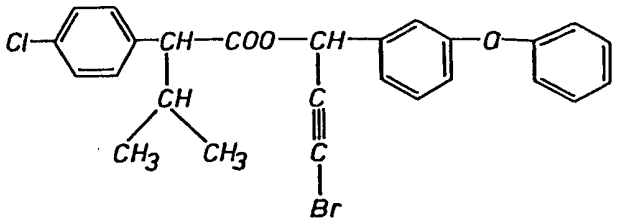
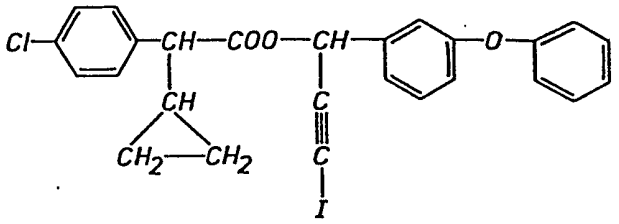
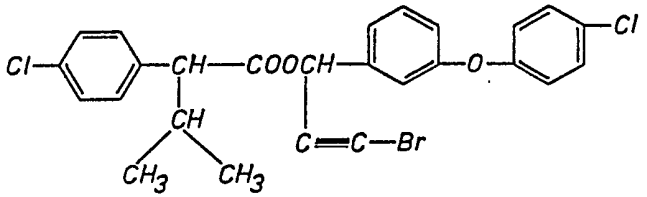
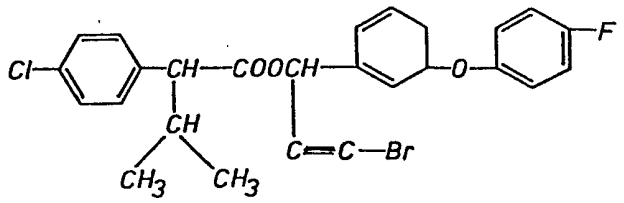
For each concentration, 5 adult ticks and 50 tick larvae, respectively, were counted into a small glass test tube, and immersed for 1 to 2 minutes in 2 ml of an aqueous emulsion from a dilution series of 100, 10, 1 and 0.1 ppm of test substance. The tubes were then sealed with a standardised cotton plug, and inverted so that the active-substance emulsion could be absorbed by the cotton wool.

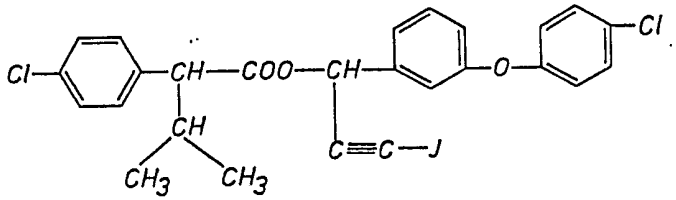
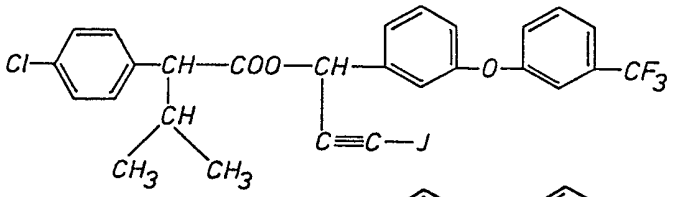
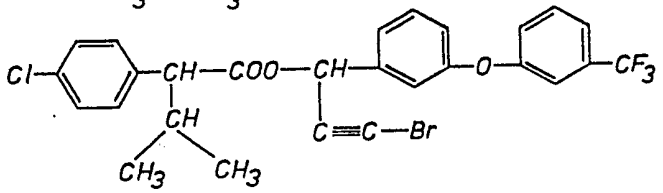
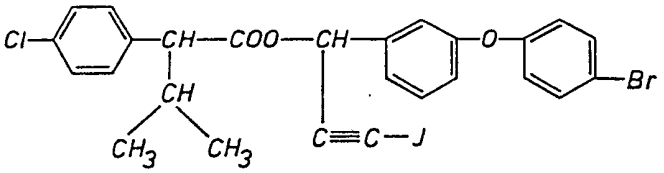
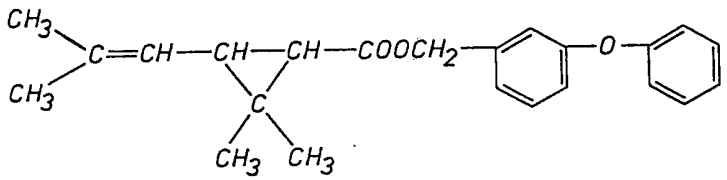
An evaluation in the case of the adults was made after 2 weeks and in the case of the larvae after 2 days. There were two repeats for each test.

b) *Boophilus microplus (larvae)*

With a dilution series analogous to that of Test a), tests were carried out with 20 sensitive larvae and OP-resistant larvae, respectively (resistance is with respect to diazinon compatibility).

Compounds according to Examples 1 to 6 were effective in these tests against adults and larvae of Rhipicephalus bursa and against sensitive and OP-resistant larvae, respectively, of Boophilus microplus.

	Minimum concentration in parts by weight of AS per 10^6 parts by weight of additives to effect a 100% mortality of			
	Spodoptera littoralis larvae	Heliothis virescens larvae	Tetranychus urticae larvae	Rhipicephalus bursa larvae
	200	200	400	10
	100	200	400	10
	200	200	400	10
	200	200	400	10

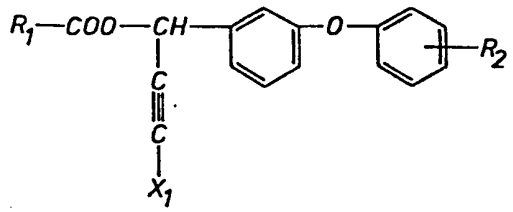
	Minimum concentration in parts by weight of AS per 10^6 parts by weight of additives to effect a 100% mortality of			
	Spodoptera littoralis larvae	Heliothis virescens larvae	Tetranychus urticae larvae	Rhipicephalus bursa larvae
	100	100	200	1
	100	100	200	1
	200	200	400	10
	100	200	200	10
	400	400	800	-

phenothrine

(Dutch Patent Specification No. 7,409,256)

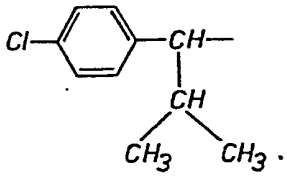
CLAIMS

1. A compound of the formula

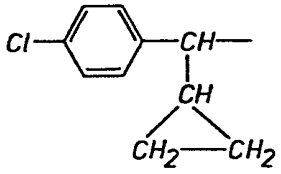


(I)

wherein R_1 is



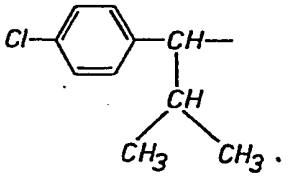
or



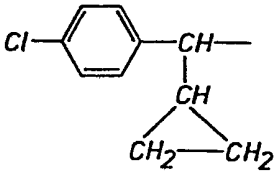
R_2 is hydrogen, fluorine, chlorine, bromine, methyl, trifluoromethyl or methoxy, and
X_1 is halogen.

2. A compound according to Claim 1, wherein

R_1 is



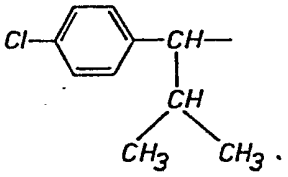
or



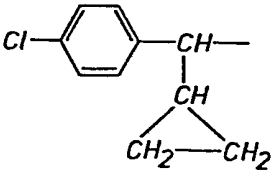
R_2 is hydrogen, fluorine, chlorine, bromine or trifluoromethyl, and
X_1 is bromine or iodine.

3. A compound according to Claim 2, wherein

R_1 is

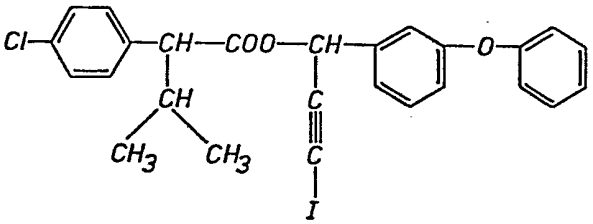


or

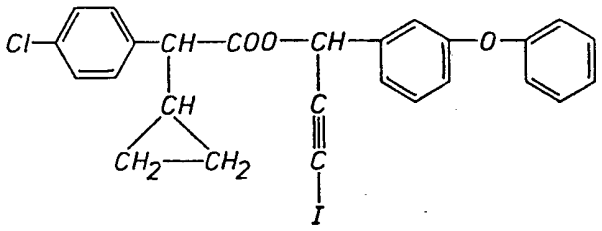


R_2 is hydrogen, and
X_1 is bromine or iodine.

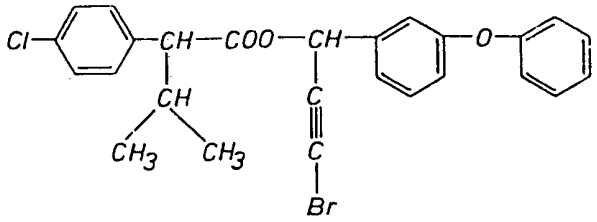
4. The compound according to Claim 3 of the formula



5. The compound according to Claim 3 of the formula



6. The compound according to Claim 3 of the formula

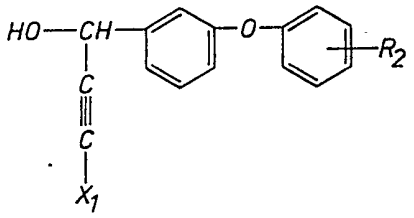


7. A compound of formula I substantially as described with reference to any of Examples 1 to 6.

8. A process for producing a compound according to Claim 1, which process comprises reacting a compound of the formula

R_1—COX

in the presence of an acid-binding agent, with the compound of the formula



wherein R_1, R_2 and X_1 have the meanings defined in Claim 1, and X is a halogen atom.

9. A process for producing a compound of formula I substantially as described with reference to any of Examples 1 to 6.

10. A compound of formula I when produced by a process claimed in claim 8 or 9.

11. A pesticidal composition which comprises a compound according to Claim 1 as active ingredient, and suitable carriers and/or other additives.

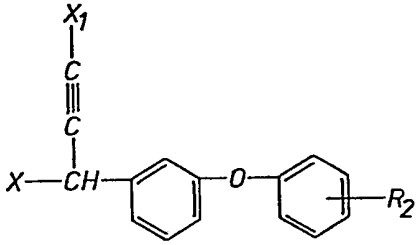
12. A pesticidal composition according to claim 11 substantially as described with reference to any of Examples 7 to 9.

13. A method of combating various animal and plant pests at a locus, which method comprises applying to the locus a compound according to Claim 1.

14. A method according to Claim 13 for combating insects, and members of the order *Acarina*.

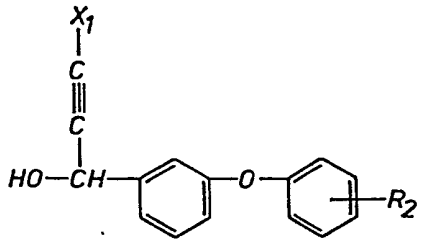
15. A method according to claim 13 substantially as described with reference to any of Examples 7 to 9.

16. A compound having the formula:



wherein R_2 and X_1 are as defined in claim 1 and X is a halogen atom.

17. A compound having the formula:



wherein R_2 and X_1 are as defined in claim 1.

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1981.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.